

FORM PTO-1390 (Modified)
(REV 10-95)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES

DESIGNATED/ELECTED OFFICE (DO/EO/US)

CONCERNING A FILING UNDER 35 U.S.C. 371

09/186

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

09/319108

INTERNATIONAL APPLICATION NO.

PCT/EP98/04055

INTERNATIONAL FILING DATE

1 July 1998

PRIORITY DATE CLAIMED

2 October 1997

TITLE OF INVENTION

SUFLINIC ACID DERIVATIVES AND THEIR PREPARATION AND USE

APPLICANT(S) FOR DO/EO/US

Josef Berghofer

Harry Rothmann

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
 - a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☐ A copy of the International Search Report (PCT/ISA/210).
8. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
9. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
10. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

Items 13 to 18 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
A **SECOND** or **SUBSEQUENT** preliminary amendment.
16. ☐ A substitute specification.
17. ☐ A change of power of attorney and/or address letter.
18. ☒ Certificate of Mailing by Express Mail
19. ☒ Other items or information:

Return postcard; Title Page; Verified Statement of Small Entity Status

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR	INTERNATIONAL APPLICATION NO. PCT/EP98/04055	ATTORNEY'S DOCKET NUMBER 99,186
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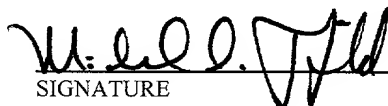
20. The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :				CALCULATIONS PTO USE ONLY	
<input type="checkbox"/> Search Report has been prepared by the EPO or JPO \$930.00 <input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) \$720.00 <input type="checkbox"/> No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) \$790.00 <input checked="" type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$1,070.00 <input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) \$98.00					
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$1,070.00	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).				\$130.00	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	22 - 20 =	2	x \$18.00	\$36.00	
Independent claims	2 - 3 =	0	x \$78.00	\$0.00	
Multiple Dependent Claims (check if applicable).			<input checked="" type="checkbox"/>	\$270.00	
TOTAL OF ABOVE CALCULATIONS =				\$1,506.00	
Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable).				<input checked="" type="checkbox"/>	\$753.00
SUBTOTAL =				\$753.00	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).				\$0.00	
TOTAL NATIONAL FEE =				\$753.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).				<input type="checkbox"/>	\$0.00
TOTAL FEES ENCLOSED =				\$753.00	
				Amount to be: refunded	\$
				charged	\$

☒ A check in the amount of **\$753.00** to cover the above fees is enclosed.

☐ Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees.
A duplicate copy of this sheet is enclosed.

☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. **13-2490** A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO: Michael S. Greenfield Reg. No. 37,142 McDonnell Boehnen Hulbert & Berghoff 300 South Wacker Drive Chicago, Illinois 60606 Phone: 312-913-0001 Fax: 312-913-0002	 SIGNATURE Michael S. Greenfield NAME 37,142 REGISTRATION NUMBER May 27, 1999 DATE
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II THE UNITED STATES PATENT AND TRADEMARK OFFICE

(Attorney's Docket No. 99,186)

Applicant or
Patent: L. Brüggemann KG

Serial or
Patent No.

Filed or
Issued:

Title: Sulfenic Acid Derivatives and Their Preparation and Use

VERIFIED STATEMENT CLAIMING SMALL ENTITY STATUS
-- (37 C.F.R. § 1.9(f) AND § 1.27(c)) - SMALL BUSINESS CONCERN

I hereby declare that I am

- ☐ the owner of the small business concern identified below:
☐ an official of the small business concern empowered to act on behalf of the concern identified below:

NAME OF CONCERN L. Brüggemann KG

ADDRESS OF CONCERN Salzstrasse 123-131, D-74076 Heilbronn, Germany

I hereby declare that the above-identified small business concern qualifies as a small business concern as defined in 13 C.F.R. § 121, and referenced in 37 C.F.R. § 1.9(d), for purposes of paying reduced fees to the United States Patent and Trademark Office, in that the number of employees of the concern, including those of its affiliates, does not exceed 500 persons. For purposes of this statement, (1) the number of employees of the business concern is the average over the previous fiscal year of the concern of the persons employed on a full-time, part-time, or temporary basis during each of the pay periods of the fiscal year, and (2) concerns are affiliates of each other when either, directly or indirectly, one concern controls or has the power to control the other, or a third party or parties controls or has the power to control both.

I hereby declare that rights under contract or law have been conveyed to and remain with the small business concern identified above with regard to the invention, entitled Sulfenic Acid Derivatives and Their Preparation and Use by inventor(s) Josef Berghofer and Harry Rothmann.

described in

☒ the specification filed herewith.
☐ Application Serial No. _____, filed _____
☐ Patent No. _____, issued _____.

If the rights held by the above identified small business concern are not exclusive, each individual concern or organization having rights in the invention must file verified statements averring to their status as small entities, and no rights to the invention are held by any person, other than the inventor, who would not qualify as an independent inventor under 37 CFR § 1.9(c) if that person made the invention, or by any concern which would not qualify as a small business concern under 37 CFR § 1.9(d), or a nonprofit organization under 37 CFR § 1.9(e).

Each person, concern or organization having any rights to the invention is listed below:

☒ No such person, concern or organization exists.

Separate verified statements are required from each named person, concern or organization having rights in the invention averring to their status as small entities. (37 CFR § 1.27).

I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee or any maintenance fee due after the date on which status as a small entity is no longer appropriate. (37 C.F.R. § 1.28(b))

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application, any patent issuing therein, or any patent to which this verified statement is directed.

NAME OF PERSON SIGNING: *Dr. Harry Rothmann*

TITLE IN ORGANIZATION: *Department Manager Industrial Chemicals*

ADDRESS OF PERSON SIGNING: *D-74076 Heilbronn, Salzstraße 123-121*

Signature: *[Signature]*

Date: *18.05.98*

L. BRÜGGEMANN & CO.
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Telefax 07131/167566

- 2 -

09/319108

510 Rec'd PCT/PTO 27 MAY 1999

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
(Case No. 99,186)

In the Application of:)
)
Berghofer and Rothmann)
) Examiner: TBA
Serial No.: TBA)
) Group Art Unit: TBA
Filing Date: Filed Concurrently Herewith)
)
For: Sulfinic Acid Derivatives and Their)
Preparation and Use)

PRELIMINARY AMENDMENT

Box New Patent Application
Asst. Commissioner for Patents
Washington, D.C. 20231

Dear Sir:

Please consider the following amendments before examination on the merits.

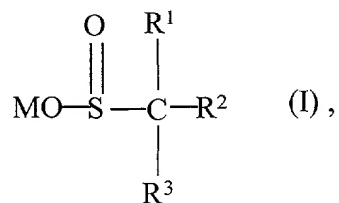
AMENDMENTS

In the claims:

Please cancel claims 20-22.

Please amend claims 1-18 as follows:

1. (Amended) A sulfinic acid compound of the formula (I)



and the salt thereof, wherein

M is a hydrogen atom, an ammonium ion, a monovalent metal ion or an equivalent of a divalent metal ion of the groups Ia, IIa, IIb, IVa or VIIIb of the Periodic Table of the Elements;

R¹ is OH or NR⁴R⁵, wherein R⁴ and R⁵ independently of one another are H or C₁-C₆-alkyl;

R² is H or an alkyl, alkenyl, cycloalkyl or aryl group, [it being possible for these groups to have] wherein the alkyl, alkenyl, cycloalkyl, and aryl group are unsubstituted or substituted with 1, 2 or 3 substituents which are chosen independently of one another from C₁-C₆-alkyl, OH, O-C₁-C₆-alkyl, halogen and CF₃; and

R³ is COOM, SO₃M, COR⁴, CONR⁴R⁵ or COOR⁴], where M, R⁴ and R⁵ are as defined above, or, if R² is aryl, which may be unsubstituted or substituted as defined above, is also H,]; or

R³ is H, provided that when R³ is H R² is unsubstituted aryl or aryl substituted with 1, 2 or 3 substituents which are chosen independently of one another from C₁-C₆-alkyl, OH, O-C₁-C₆-alkyl, halogen and CF₃.

[and the salt thereof.]

2. (Amended) [A] The sulfinic acid compound as claimed in claim 1 [of the formula (I)], wherein

M is an ammonium or alkali metal ion or an equivalent of an alkaline earth metal ion or zinc ion.

3. (Amended) [A] The sulfinic acid compound as claimed in claim 1 [or 2 of the formula (I)], wherein

R¹ is OH or NH₂.

4. (Amended) [A] The sulfinic acid compound as claimed in claim 1 [of the formula (I)],
wherein

R^2 is a hydrogen atom or an alkyl or aryl group which [may have] are unsubstituted or substituted with one or two hydroxyl or alkoxy substituents.

5. (Amended) [A] The sulfinic acid compound as claimed in claim 1 [of the formula (I)],
wherein

R^3 is COOM or COOR⁴ [, where M and R⁴ are as defined in claim 1].

6. (Amended) [A] The sulfinic acid compound as claimed in claim 1 [of the formula (I)],
wherein

M is an alkali metal ion or an equivalent of an alkaline earth metal ion or zinc ion;

R^1 is OH or NH₂;

R^2 is H or alkyl; and

R^3 is COOM or COOR⁴, [M being as defined above and] wherein R⁴ [being] is H or C₁-C₆-alkyl.

7. (Amended) [A] The sulfinic acid compound as claimed in claim 4 [of the formula (I)],
wherein

R^2 is aryl, which [may have] is unsubstituted or substituted with one or two hydroxyl or alkoxy substituents; and

R^3 is H.

8. (Amended) [A] The sulfinic acid compound as claimed in claim 7 [of the formula (I)],
wherein

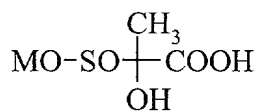
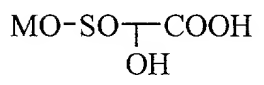
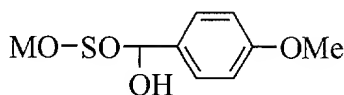
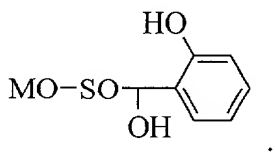
R^2 is hydroxyphenyl or C₁-C₄-alkoxyphenyl.

9. (Amended) [A] The sulfinic acid compound as claimed in claim 1 [of the formula (I)],
wherein

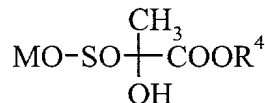
M is an alkali metal ion or an equivalent of an alkaline earth metal ion or zinc ion;

- R^1 is OH or NH_2 ;
 R^2 is hydroxyphenyl or C_1 - C_4 -alkoxyphenyl; and
 R^3 is a hydrogen atom.

10. (Amended) [Compounds] A compound of the formulae [(M = Na, K, Mg, Ca, Zn)]:



or



wherein M is Na, K, Mg, Ca, Zn and R^4 is CH_3 or C_2H_5 .

11. (Amended) [A] The mixture of a sulfinic acid compound as claimed in one of claims 1 to 10 with the sulfonic acid corresponding to the sulfinic acid compound or the salt thereof and with or without the corresponding sulfite.

12. (Amended) [A] The mixture as claimed in claim 11 having the following composition:

Compound of the formula (I)	20-99% by weight
Sulfonic acid corresponding to the compound of formula (I)	0-60% by weight
M_2SO_3	0-40% by weight

13. (Amended) [A] The mixture as claimed in claim 12 having the following composition:

2-Hydroxyphenylhydroxymethylsulfinic acid, sodium salt:	61-98% by weight
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2-Hydroxyphenylhydroxymethylsulfonic
acid, sodium salt: 2-15% by weight
Sodium sulfite: 0-37% by weight

14. (Amended) [A] The mixture as claimed in claim 12 having the following composition:

4-Methoxyphenylhydroxymethylsulfinic
acid, sodium salt: 60-98% by weight
4-Methoxyphenylhydroxymethylsulfonic
acid, sodium salt: 2-15% by weight
Sodium sulfite: 0-38% by weight

15. (Amended) [A] The mixture as claimed in claim 12 having the following composition:

2-Hydroxy-2-sulfinatoacetic acid,
disodium salt: 40-73% by weight
2-Hydroxy-2-sulfonatoacetic acid,
disodium salt: 2-7% by weight
Sodium sulfite: 0-33% by weight
Water: 5-30% by weight

16. (Amended) [A] The mixture as claimed in claim 12 having the following composition:

2-Hydroxy-2-sulfinatoacetic acid,
zinc salt: 20-70% by weight
2-Hydroxy-2-sulfonatoacetic acid,
zinc salt: 5-60% by weight
water: 5-30% by weight

17. (Amended) [A] The mixture as claimed in claim 12 having the following composition:

2-Hydroxy-2-sulfinatopropionic acid,
disodium salt: 38-70% by weight
2-Hydroxy-2-sulfonatopropionic acid,

disodium salt: 5-30% by weight
Sodium sulfite: 0-33% by weight
Water: 5-30% by weight

18. (Amended) [A] The mixture as claimed in claim 12 having the following composition:

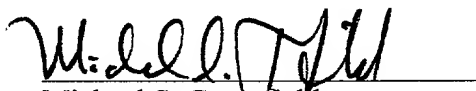
Ethyl 2-hydroxy-2-sulfinatopropionate,
sodium salt: 60-80% by weight
Ethyl 2-hydroxy-2-sulfonatopropionate,
sodium salt: 0-5% by weight
Sodium sulfite: 0-5% by weight
Water: 5-20% by weight.

Please add new claims 23-25.

23. (New) A method of reducing a chemical compound, the method comprising contacting the compound with a sulfinic acid compound according to any one claims 1-10 under conditions that permit reduction.
24. (New) The method according to claim 24, wherein the sulfinic acid compound is a cocatalyst in emulsion polymerization or redox catalyst system in plastics production.
25. (New) The method according to claim 24, wherein the sulfinic acid compound is a reducing agent component for textile printing, in textile bleaching or vat dyeing or a reducing bleach for mineral refining or fiber finishing.

Respectfully submitted,

Date: May 27, 1999



Michael S. Greenfield
Registration No. 37,142

	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026	2027	2028	2029	2030	2031	2032	2033	2034	2035	2036	2037	2038	2039	2040	2041	2042	2043	2044	2045	2046	2047	2048	2049	2050	2051	2052	2053	2054	2055	2056	2057	2058	2059	2060	2061	2062	2063	2064	2065	2066	2067	2068	2069	2070	2071	2072	2073	2074	2075	2076	2077	2078	2079	2080	2081	2082	2083	2084	2085	2086	2087	2088	2089	2090	2091	2092	2093	2094	2095	2096	2097	2098	2099	2100																																																																																																			
1.000000	0.999999	0.999998	0.999997	0.999996	0.999995	0.999994	0.999993	0.999992	0.999991	0.999990	0.999989	0.999988	0.999987	0.999986	0.999985	0.999984	0.999983	0.999982	0.999981	0.999980	0.999979	0.999978	0.999977	0.999976	0.999975	0.999974	0.999973	0.999972	0.999971	0.999970	0.999969	0.999968	0.999967	0.999966	0.999965	0.999964	0.999963	0.999962	0.999961	0.999960	0.999959	0.999958	0.999957	0.999956	0.999955	0.999954	0.999953	0.999952	0.999951	0.999950	0.999949	0.999948	0.999947	0.999946	0.999945	0.999944	0.999943	0.999942	0.999941	0.999940	0.999939	0.999938	0.999937	0.999936	0.999935	0.999934	0.999933	0.999932	0.999931	0.999930	0.999929	0.999928	0.999927	0.999926	0.999925	0.999924	0.999923	0.999922	0.999921	0.999920	0.999919	0.999918	0.999917	0.999916	0.999915	0.999914	0.999913	0.999912	0.999911	0.999910	0.999909	0.999908	0.999907	0.999906	0.999905	0.999904	0.999903	0.999902	0.999901	0.999900	0.999899	0.999898	0.999897	0.999896	0.999895	0.999894	0.999893	0.999892	0.999891	0.999890	0.999889	0.999888	0.999887	0.999886	0.999885	0.999884	0.999883	0.999882	0.999881	0.999880	0.999879	0.999878	0.999877	0.999876	0.999875	0.999874	0.999873	0.999872	0.999871	0.999870	0.999869	0.999868	0.999867	0.999866	0.999865	0.999864	0.999863	0.999862	0.999861	0.999860	0.999859	0.999858	0.999857	0.999856	0.999855	0.999854	0.999853	0.999852	0.999851	0.999850	0.999849	0.999848	0.999847	0.999846	0.999845	0.999844	0.999843	0.999842	0.999841	0.999840	0.999839	0.999838	0.999837	0.999836	0.999835	0.999834	0.999833	0.999832	0.999831	0.999830	0.999829	0.999828	0.999827	0.999826	0.999825	0.999824	0.999823	0.999822	0.999821	0.999820	0.999819	0.999818	0.999817	0.999816	0.999815	0.999814	0.999813	0.999812	0.999811	0.999810	0.999809	0.999808	0.999807	0.999806	0.999805	0.999804	0.999803	0.999802	0.999801	0.999800	0.999799	0.999798	0.999797	0.999796	0.999795	0.999794	0.999793	0.999792	0.999791	0.999790

**Inventors: Josef Berghofer
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D-74080 Jeilbronn
Germany**

Harry Rothmann
Tulpenstrasse 28 a
D-74915 Daisbach
Germany

**Sulfinic acid derivatives and their
preparation and use**

The invention relates to sulfinic acid derivatives and
5 their preparation and use in various application areas.

As is known, sulfinic acid, H_2SO_2 , is one of the
strongest known reducing agents. The free sulfinic acid
is unstable. Accordingly, it is only available commer-
10 cially in the form of its stable and correspondingly
manageable derivatives.

The following sulfinic acid derivatives have to date
achieved economic importance:

15

1. Sodium dithionite (fiber bleaching in papermaking,
vat dyeing and textile bleaching, mineral
bleaching, heavy metal reduction in industrial
wastewaters)
- 20 2. Sodium formaldehyde sulfoxylate dihydrate (textile
discharge printing, textile bleaching, redox
cocatalyst in emulsion polymerization, heavy-metal
reduction, pharmaceuticals)
3. Formamidinesulfinic acid (fiber bleaching in
25 papermaking, textile bleaching)
4. Zinc formaldehyde sulfoxylate (textile printing
and textile bleaching)

All of the abovementioned sulfinic acid derivatives are
30 used in the form of aqueous solutions or dispersions.
In aqueous media, sodium dithionite and alkali metal
formamidinesulfinate - the free formamidinesulfinic
acid is virtually insoluble in water and, in its acid
form, has only a very slight reducing action - are only
35 stable for a short time. As a result, even at room
temperature they exhibit an excellent reductive

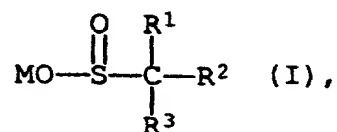
capacity and an excellent bleaching effect on fibers. Aqueous preparations of sodium formaldehyde sulfoxylate and of zinc formaldehyde sulfoxylate are stable at room temperature for months. As a result, both formaldehyde sulfoxylates only exhibit their true reducing action at temperatures above 90° Celsius. In strongly alkaline or acidic media or in the presence of suitably strong oxidizing agents, both formaldehyde sulfoxylates do of course also have a reducing effect at temperatures lower than 90°C. This particular property of the formaldehyde sulfoxylates, namely to exhibit a very uniform and easily controlled reducing effect at temperatures between 5°C and 90°C, is made use of in free-radical-initiated emulsion polymerization. Here, the formaldehyde sulfoxylates are used in various emulsion polymerization systems. In the case of the cold preparation of SBR (styrene butadiene rubber), the polymerization is initiated using organic peroxides. At the low polymerization temperature of about 5°C, the organic peroxides do not, however, decompose into the required free radicals. The peroxide cleavage must be initiated by catalytic amounts of iron(II) salts. The iron in oxidation stage two is converted into oxidation stage three making it no longer suitable for the peroxide cleavage. With the help of the formaldehyde sulfoxylate, the iron(III) ions are again reduced to iron(II) ions - the peroxide cleavage and the free-radical initiation continues. In other emulsion polymerization systems, peroxide compounds, such as hydrogen peroxide or peroxodisulfate, are used as free-radical formers. In order to increase the rate of free-radical formation, reducing agents are again used. Examples which may be mentioned are formaldehyde sulfoxylates, bisulfites, ascorbic acid, isoascorbic acid and sodium erythrobate. Formaldehyde sulfoxylates, in particular sodium

formaldehyde sulfoxylate, have proven to be particularly effective and good value reducing agents. During the reduction process, however, the formaldehyde sulfoxylates eliminate formaldehyde. Plastics or
5 polymer dispersions which must not contain formaldehyde are polymerized either using bisulfites, ascorbic acid, isoascorbic acid or sodium erythroate. Since the formaldehyde-free reducing agents are weaker reducing agents, the disadvantage of less complete
10 polymerization compared with formaldehyde sulfoxylates must be accepted. Furthermore, the use of ascorbic acid, isoascorbic acid and of sodium erythroate leads to an undesired yellowing of the polymer.

15 The object of the present invention is to provide novel sulfinic acid derivatives whose chemical properties are as similar as possible to those of formaldehyde sulfoxylate, but which do not eliminate formaldehyde during or after use.

20 Surprisingly, it has now been found that this object is achieved by sulfinic acid derivatives of the type described in more detail below.

25 The present invention thus provides sulfinic acid compounds of the formula (I):



where

30 M is a hydrogen atom, an ammonium ion, a monovalent metal ion or an equivalent of a divalent metal ion of the groups Ia, IIa, IIb, IVa or VIIIB of the Periodic Table of the Elements;

R¹ is OH or NR⁴R⁵, where R⁴ and R⁵ independently of one another are H or C₁-C₆-alkyl;

R² is H or an alkyl, alkenyl, cycloalkyl or aryl group, it being possible for these groups to have 1, 2 or 3 substituents which are chosen independently of one another from C₁-C₆-alkyl, OH, O-C₁-C₆-alkyl, halogen and CF₃; and

R³ is COOM, SO₃M, COR⁴, CONR⁴R⁵ or COOR⁴, where M, R⁴ and R⁵ are as defined above, or, if R² is aryl, which may be unsubstituted or substituted as defined above, R³ is also H,

and the salts thereof.

For the purposes of the present invention, the expressions listed below have the following meanings:

Alkyl represents straight-chain or branched alkyl groups which preferably have 1-6, in particular 1-4, carbon atoms. Examples of alkyl groups are methyl, ethyl, n-propyl, isopropyl, n-butyl, t-butyl, n-hexyl, etc.

The same applies to the alkyl groups in O-alkyl.

Alkenyl represents straight-chain or branched alkenyl groups which preferably have 3-8 carbon atoms, in particular 3-6 carbon atoms. A preferred alkenyl group is the allyl group.

Cycloalkyl is, in particular, C₃-C₆-cycloalkyl, cyclopentyl and cyclohexyl being particularly preferred.

Aryl (also in aralkyl) is preferably phenyl or naphthyl. If the aryl radical is a phenyl group and is

substituted, it preferably has two substituents. These are, in particular, in the 2- and/or 4-position.

Halogen represents F, Cl, Br and I, preferably Cl and Br.

M is preferably an ammonium ion, alkali metal ion or an equivalent of an alkaline earth metal ion or zinc ion. Suitable alkali metal ions are, in particular, sodium and potassium ions. Suitable alkaline earth metal ions are in particular magnesium and calcium ions.

R^1 is preferably a hydroxyl or amino group.

R^2 is preferably a hydrogen atom or an alkyl or aryl group which may be substituted as above. It preferably has one or two hydroxyl and/or alkoxy substituents.

R^3 is preferably either COOM or COOR⁴ (M and R⁴ are as defined above) or, if R^2 is aryl, which may be substituted as stated above, may also be a hydrogen atom.

A preferred embodiment covers compounds of the formula (I) in which

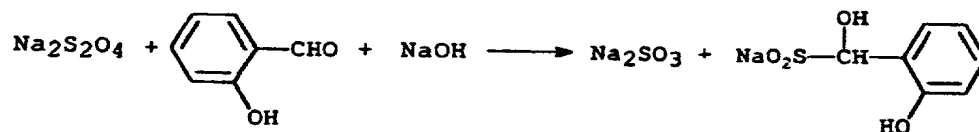
M is an alkali metal ion or an equivalent of an alkaline earth metal ion or zinc ion;
 R^1 is a hydroxyl or amino group; R^2 is H or alkyl; and
 R^3 is COOM or COOR⁴, where M is H, an alkali metal ion or an equivalent of an alkaline earth metal ion, and R^4 is C₁-C₆-alkyl.

A further preferred embodiment covers compounds of the formula (I), in which

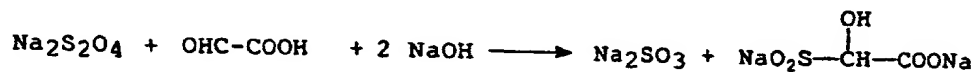
M is an alkali metal ion or an equivalent of an alkaline earth metal ion or zinc ion;

- R^1 is a hydroxyl or amino group;
 R^2 is an unsubstituted aryl or aryl substituted as stated above, in particular hydroxyphenyl or C_1 - C_4 -alkoxyphenyl; and
 5 R_3 is a hydrogen atom.

The novel compounds are prepared from dithionite salts. Advantageously, a salt having a cation which is also desired in the sulfinic acid compounds is used. The
 10 dithionite salts are reacted by preparing those compounds in which R^2 is an unsubstituted or substituted aryl radical and R^3 is a hydrogen atom, with the corresponding aromatic aldehyde. This reaction can be illustrated using sodium dithionite and 2-hydroxy-
 15 benzaldehyde as an example by the following reaction equation:



All other compounds of the formula M are prepared by reacting the dithionite salts with the corresponding
 20 1,2-dicarbonyl compound or a sulfonic acid equivalent thereof. The 1,2-dicarbonyl compound used is, in particular, glyoxylic acid or the corresponding keto compounds and their esters. The reaction can be illustrated using sodium dithionite and glyoxylic acid
 25 as an example by the reaction equation below:



The reaction is generally carried out in an aqueous medium in the presence of a base. The aqueous medium may also include water-soluble organic solvents, such
 30 as methanol, ethanol, isopropanol, etc. Bases which may be used are, in particular, alkali metal hydroxides and

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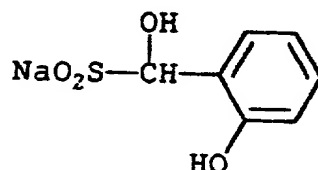
undesired. For example, they can be used as reducing agents in textile printing, in particular in textile discharge printing, in textile bleaching or vat dyeing, or as reducing agents for bleaching minerals, such as kaolin etc., and fibers, for example cellulose fibers. They are preferably used, however, as cocatalyst in emulsion polymerization together with peroxidic initiators in order to allow the polymerization to be carried out at a lower temperature. For this purpose, the sulfinic acids may, if desired, be also used together with oxidizable metal ions, such as Fe^{2+} , Mn^{2+} etc. These metal ions are then advantageously used as counterions to the sulfinic acid compounds, i.e. $\text{M} = \text{Fe}^{2+}$, Mn^{2+} etc.

For use, the novel compounds are generally formulated together with customary additives and auxiliaries. There is no particular limitation in this respect, only that reducing compounds must not be used.

The examples below illustrate the invention without limiting it. The purity figures given in the examples refer to the product which contains water of crystallization which is produced, i.e. the purity is significantly higher when the content of water of crystallization is taken into consideration.

Example 1

2-Hydroxyphenylhydroxymethylsulfinic acid, sodium salt

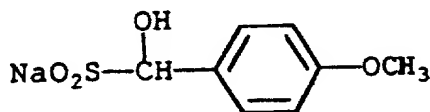


50 ml of 2-hydroxybenzaldehyde and 45 g of 50% strength sodium hydroxide solution were added to an aqueous solution of 90 g of commercially available sodium hydrosulfite (sodium dithionite). After the exothermic reaction had finished, the resulting crude product was separated off using methanol and recrystallized from a methanol/ethanol/water mixture. The 2-hydroxyphenylhydroxymethylsulfonic acid, sodium salt was produced with a purity of 75.8%. The sulfinic acid content was determined using iodometry. The IR spectroscopic data (T = transmission) are as follows:

3551.97 cm^{-1} (28.51 %T); 3175.96 cm^{-1} (19.45 %T); 2915.51 cm^{-1} (29.95 %T); 2747.10 cm^{-1} (34.58 %T); 1899.95 cm^{-1} (61.96 %T); 1682.34 cm^{-1} (44.77 %T); 1641.40 cm^{-1} (38.98 %T); 1594.46 cm^{-1} (32.49 %T); 1505.02 cm^{-1} (42.21 %T); 1455.65 cm^{-1} (17.74 %T); 1387.05 cm^{-1} (27.73 %T); 1330.41 cm^{-1} (40.37 %T); 1280.09 cm^{-1} (30.89 %T); 1244.74 cm^{-1} (23.14 %T); 1200.40 cm^{-1} (31.90 %T); 1155.73 cm^{-1} (30.12 %T); 1111.53 cm^{-1} (29.83 %T); 1098.58 cm^{-1} (32.10 %T); 1072.68 cm^{-1} (28.14 %T); 1030.15 cm^{-1} (16.57 %T); 995.68 cm^{-1} (16.40 %T); 957.46 cm^{-1} (16.83 %T); 872.69 cm^{-1} (43.53 %T); 846.84 cm^{-1} (42.51 %T); 801.62 cm^{-1} (40.51 %T); 762.15 cm^{-1} (28.82 %T); 744.61 cm^{-1} (21.25 %T); 659.92 cm^{-1} (26.13 %T); 629.31 cm^{-1} (30.85 %T); 588.96 cm^{-1} (26.78 %T); 561.45 cm^{-1} (41.13 %T); 496.95 cm^{-1} (30.36 %T).

Example 2

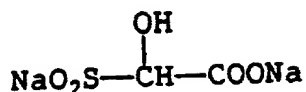
4-Methoxyphenylhydroxymethylsulfonic acid, sodium salt



63 g of 4-methoxybenzaldehyde and 45 g of 50% strength aqueous sodium hydroxide solution were added to 90 g of commercially available sodium hydrosulfite in aqueous solution. Evaporation of the resulting solution precipitated out the crude product. The sodium salt of the sulfinic acid was obtained by crystallization from a methanol/ethanol/water mixture having a purity of 68%. The sodium salt of the corresponding sulfonic acid was present as a secondary constituent.

Example 3

2-Hydroxy-2-sulfinatoacetic acid, disodium salt



The reaction of 358 g of commercially available sodium hydrosulfite in 800 ml of water with 268 g of 50% strength glyoxylic acid and 285 g of 50% sodium hydroxide solution gave the 2-hydroxy-2-sulfinatoacetic acid, disodium salt in a yield of 95%. The solid crude product contained 43% of sulfinic acid (without water of hydration). Crystallization from a methanol/ethanol/water mixture gave the hydrate of the sulfinic acid in nice crystals. The sulfur-containing constituents were determined using iodometry. The sulfinic acid shows a reaction with indanthrene paper at about 75°C.

The IR spectrum shows the following peaks:

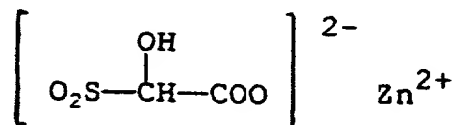
3588.57 cm^{-1} (6.21 %T); 3485.05 cm^{-1} (1.37 %T); 3339.44 cm^{-1} (1.75 %T); 2905.13 cm^{-1} (38.46 %T); 2794.17 cm^{-1} (42.39 %T); 2189.93 cm^{-1} (54.06 %T); 1662.54 cm^{-1} (7.35 %T); 1613.92 cm^{-1} (0.67 %T); 1417.54 cm^{-1} (7.34 %T); 1388.03 cm^{-1} (8.65 %T); 1248.31 cm^{-1} (3.95 %T); 1185.34 cm^{-1} (30.75 %T); 1153.96 cm^{-1} (20.95 %T); 1103.16 cm^{-1} (5.58 %T); 1027.04 cm^{-1} (2.61 %T); 968.33 cm^{-1} (1.77 %T); 938.07 cm^{-1} (26.60 %T); 847.72 cm^{-1} (23.10 %T); 717.14 cm^{-1} (10.46 %T); 645.46 cm^{-1} (14.88 %T); 541.36 cm^{-1} (9.25 %T); 491.77 cm^{-1} (11.95 %T); 445.88 cm^{-1} (19.22 %T)

^{13}C nuclear magnetic resonance spectrum (63 MHz):

δ (ppm): 93.8 (s) ; 177.7 (s)

Example 4

2-Hydroxy-2-sulfinatoacetic acid, zinc salt

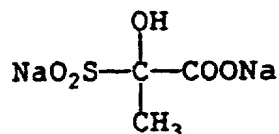


The reaction of 33 g of Zn dust in aqueous medium with sulfur dioxide gave zinc dithionite. This was reacted in situ with 136 g of 50% strength glyoxylic acid.

After the exothermic reaction had finished, 75 g of ZnO were added. The crude product present in the filtrate was precipitated out using methanol and comprised 20% of sulfinic acid and 48% of sulfonic acid (iodometric determination).

Example 5

2-Hydroxy-2-sulfinatopropionic acid, disodium salt



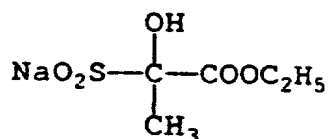
- 10 Starting from 89 g of commercially available sodium hydrosulfite in water, the crude product was obtained by reaction with 40 g of pyruvic acid and about 78 g of 50% strength sodium hydroxide solution. The crude product comprised 40% of sulfinic acid and was
- 15 recrystallized from a methanol/ethanol/water mixture. The content was determined iodometrically. The disodium salt of the corresponding sulfonic acid was present as a secondary constituent.

The IR spectroscopic signals found were as follows:

3484.66 cm^{-1} (6.25 %T); 2995.53 cm^{-1} (26.51 %T); 2758.93 cm^{-1} (32.54 %T); 1592.63 cm^{-1} (0.62 %T); 1456.02 cm^{-1} (16.06 %T); 1436.19 cm^{-1} (17.02 %T); 1397.00 cm^{-1} (4.77 %T); 1367.01 cm^{-1} (7.14 %T); 1190.80 cm^{-1} (2.49 %T); 1038.50 cm^{-1} (0.70 %T); 981.07 cm^{-1} (1.42 %T); 943.83 cm^{-1} (7.90 %T); 857.07 cm^{-1} (20.25 %T); 804.64 cm^{-1} (32.86 %T); 790.68 cm^{-1} (34.62 %T); 710.08 cm^{-1} (30.79 %T); 659.00 cm^{-1} (11.96 %T); 628.53 cm^{-1} (9.93 %T); 558.19 cm^{-1} (26.14 %T); 522.56 cm^{-1} (16.21 %T); 497.03 cm^{-1} (15.70 %T); 431.34 cm^{-1} (28.83 %T).

Example 6

Ethyl 2-hydroxy-2-sulfinatopropionate, sodium salt



After 90 g of commercially available sodium hydrosulfite in aqueous solution had reacted with 60 g of ethyl pyruvate and 39 g of 50% strength sodium hydroxide solution, the ethyl 2-hydroxy-2-sulfinato-propionate, sodium salt precipitated out during the exothermic reaction as the hydrate. The separated off and dried crude product comprises 79% of sulfinic acid (calculated without water of crystallization). The contents were determined using iodometry. The IR spectroscopic signals can be summarized as follows:

3501.08 cm^{-1} (12.01 %T); 3328.38 cm^{-1} (16.14 %T); 3003.23 cm^{-1} (51.87 %T); 2986.52 cm^{-1} (45.03 %T); 2940.61 cm^{-1} (54.87 %T); 1733.45 cm^{-1} (7.42 %T); 1663.31 cm^{-1} (48.05 %T); 1469.00 cm^{-1} (32.01 %T); 1402.22 cm^{-1} (42.89 %T); 1367.58 cm^{-1} (40.81 %T); 1298.47 cm^{-1} (43.49 %T); 1262.97 cm^{-1} (26.65 %T); 1190.27 cm^{-1} (10.52 %T); 1105.86 cm^{-1} (10.94 %T); 1038.98 cm^{-1} (6.62 %T); 1012.00 cm^{-1} (30.53 %T); 985.42 cm^{-1} (9.37 %T); 948.69 cm^{-1} (28.55 %T); 860.86 cm^{-1} (56.24 %T); 801.55 cm^{-1} (61.53 %T); 685.30 cm^{-1} (51.65 %T); 658.49 cm^{-1} (51.18 %T); 590.17 cm^{-1} (34.18 %T); 523.55 cm^{-1} (34.88 %T); 471.89 cm^{-1} (41.25 %T); 425.61 cm^{-1} (59.75 %T).

Example 7

For the textile discharge printing on a black fabric, a printing paste having the following formulation was chosen.

Base formulation of the printing paste:

- 434 g of water
- 100 g of potash
- 6 g of KL 100 thickener (carboxymethylated starch)
- 40 g of Lameprint IND8 (guar ether + starch ether)
- 14 g of glycerol
- 6 g of Printogen (self-emulsifying mineral oil)

600 g of base formulation

The formaldehyde-free reducing agent corresponding to Example 3 or sodium formaldehyde sulfoxylate for the comparative mixture were then added to this base

formulation.

Mixture 1	Comparative mixture
600 g of base formulation	600 g of base formulation
213 g of 2-hydroxy-2-sulfinatoacetic acid, disodium salt corresponding to Example 3 (crude product)	107 g of sodium formaldehyde sulfoxylate

The resulting mixtures were then applied to the black fabric next to one another and dried in a drying cabinet. The fabric was then aged at 102°C for 10 minutes, during which time the dye was reduced. The fabric was thoroughly rinsed to remove residues of thickener and other chemicals, and the undyed fabric became apparent at those places where the reducing agent had previously been applied.

It is evident that the discharge printing has performed well. The rinsing of the preparations presented no problems of any kind. The disodium salt of 2-hydroxy-2-sulfinatoacetic acid can thus be used in textile discharge printing according to current technology. The results of the discharge printing are summarized in Table 1:

Table 1:

Whiteness R457	Mixture 1	Comparative Mixture
1st measurement	69.55	71.40
2nd measurement	70.24	70.73
1st yellowness index	9.83	8.91
2nd yellowness index	9.51	9.05

Example 8

Bleaching of kaolin

The starting concentration of the kaolin was 250 g/l.

The slurry had a pH of 6.5. After the kaolin suspension had been homogenized using a stirrer for 30 minutes, the pH was adjusted to 2.5 using semi-concentrated sulfuric acid.

5

The disodium salt of 2-hydroxy-2-sulfinatoacetic acid corresponding to Example 3 and sodium formaldehyde sulfoxylate were added as 10% strength solutions and were based on the solids content of the kaolin suspension (see Table 2).

10

Reaction conditions:

Temperature: Room temperature

pH: 2.5

15 Reaction time: 2 hours

Table 2:

Kaolin type	Feed amount	Initial whiteness [%]	Final whiteness [%]	Shade	Saturation
	[% , absolutely dry]	R 457	R 457	R 457	R 457
A	0.45 of the disodium salt of 2-hydroxy-2-sulfinatoacetic acid corresponding to Example 3	73.4	76.8	1.51	0.46
A	0.3 of sodium formaldehyde sulfoxylate	73.4	74.5	1.59	0.61
B*	0.3 of the disodium salt of 2-hydroxy-2-sulfinatoacetic acid corresponding to Example 3	79.5	82.5	1.02	0.34
B	0.3 of sodium formaldehyde sulfoxylate	79.5	79.7	1.34	0.46

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* Sodium pyrophosphate was added as complexing agent.

5 The preparation containing the disodium salt of 2-hydroxy-2-sulfinatoacetic acid produces good results in the bleaching of kaolin. The preparation containing the disodium salt of hydroxyacetylsulfinic acid reacted 3-4 times more quickly than the sodium formaldehyde sulfoxylate. The use in the bleaching of minerals, in particular for kaolin, is possible according to current technology.

Example 9 (Comparative example)

15 400 g of water, 286 g of a 10% strength aqueous solution of Airvol 205 (polyvinyl alcohol, 88% hydrolysed; DP = 500; manufactured by Air Products and Chemicals, Inc.), 286 g of a 10% strength aqueous solution of Airvol 107 (polyvinyl alcohol, 98% hydrolysed; DP = 500; manufactured by Air Products and Chemicals, Inc.) and 47 g of Igepal CO-887 (nonionic surfactant, manufactured by Rhone-Poulenc, Inc.; 70% strength aqueous solution of Igepal CO-880 comprises approximately 30 mol of ethylene oxide) were charged to a 3.8 liter pressurized reactor and mixed with 4.8 g of a 1% strength aqueous iron(II) sulfate solution. The reaction mixture was adjusted to a pH of 3.3 using 1.75 g of a 50% strength phosphoric acid solution. 1710 g of vinyl acetate monomer were then metered in.

25 The reaction mixture was stirred at 900 rpm and heated to 35°C. 200 g of gaseous ethylene were then introduced at a pressure up to 20.4 atm. 5.7 g of a 10% strength aqueous solution of isoascorbic acid (pH = 4) having the following composition:

35 270 g of water

30 g of isoascorbic acid

0.8 g of 29% strength ammonium hydroxide solution, were then added. The polymerization was initiated using a total of 10 g of 0.65% strength aqueous hydrogen peroxide solution having the following composition:

589 g of deionized water

11.1 g of 35% strength hydrogen peroxide.

After the polymerization had been initiated, the remaining 295.1 g of the ammonium isoascorbate/isoascorbic acid solution were metered in over the course of 4 hours. The remaining 590.1 g of 0.65% strength hydrogen peroxide solution were added to control the polymerization such that the reaction mixture warmed up from 35°C to 55°C over a period of 1 hour and such that the reaction mixture could then be maintained at 55°C for 3 hours. After a total polymerization time of 4 hours, the content of free vinyl acetate monomer was still 1.5%.

The reaction mixture was cooled to 35°C and transferred to a pressureless reactor in order to degas excess ethylene. The free vinyl acetate monomer remaining in the emulsion was subsequently polymerized by the addition of 20 g of a 10% strength aqueous isoascorbic acid solution and a 3.5% strength hydrogen peroxide solution and as a result forced down to a final content below 0.5% of free vinyl acetate monomer. The pH of the polymer emulsion was adjusted to the desired pH (see Table 3) using a 14% strength aqueous ammonium hydroxide solution. The physical properties of the polymer emulsion (latex) are summarized in Table 3.

Example 10 (Comparative example)

The emulsion polymerization as in Example 9 was repeated, and in place of the ammonium isoascorbate/isoascorbic acid, an aqueous solution

consisting of 270 g of water and 22.1 g of sodium formaldehyde sulfoxylate was used. The results are summarized in Table 3.

- 5 Example 11 (cocatalyst in the emulsion polymerization)
The emulsion polymerization as in Example 9 was repeated, and in place of the ammonium isoascorbate/isoascorbic acid, an aqueous solution consisting of 270 g of water and 33 g of reducing agent according to
- 10 Example 3 (crude product) was used. The results are summarized in Table 3.

Table 3

Parameter of the resulting latices	Example 9 (Comparison)	Example 10 (Comparison)	Example 11 (Invention)
Appearance	slightly yellowish	milky white	milky white
Solids content [%]	62.1	63.4	63.2
pH	6.5	6.0	6.2
Viscosity [Pa·s] (60 rpm; 25°C)	440	380	560
Tg (polymer) [°C]	+5	+4	+7
free formaldehyde [ppm]	-	130	-

- 15 Example 12
Groundwood bleaching
Conditions for the groundwood bleaching:
Stock consistency: 5.4%
Bleaching temperature: 75°C
- 20 Bleach addition: 0.2/0.4/0.6/0.8/1.0% of bleach,
absolutely dry (based on dry weight)

Bleaching time: 30 minutes

For the bleaching, 100 g of groundwood were in each case weighed into polyethylene bags. To add the bleach, aqueous solutions were prepared (1 ml of these solutions comprised 0.2% of each bleach absolutely dry). After the bleach solution had been pipetted in, the bags were immediately tied up, and the contents were thoroughly mixed by kneading the closed bags. The bleaching temperature was regulated using a thermostat (water bath).

After the required bleaching time, the pulp slurry was transferred to measuring flasks and the pH after bleaching was measured. The volume was then made up to 300 ml with tap water and the mixture was homogenized by stirring the pulp slurry. The sheets were formed using a customary suction sheet former using the entire pulp slurry. The resulting sheets were vacuum-dried in the sheet former for 12 minutes.

The whiteness R457 of all of the sheets formed was determined using a whiteness measuring device (Elrepho 2000 from Datacolor). The results are summarized in Table 4.

Table 4

Bleach	Amount of bleach [% ,absolute ly dry]	Initial pH	Final pH	Whiteness	Whiteness increase ¹⁾
	0.0	6.4	6.3	65.1	-
Sodium	0.2	6.4	6.2	66.6	1.5
formalde-	0.4	6.4	6.2	66.9	1.8
hyde	0.6	6.4	6.2	67.0	1.9
sulfoxylate	0.8	6.4	6.2	67.3	2.2
	1.0	6.4	6.2	67.7	2.6
Disodium salt	0.0	6.5	6.4	65.7	-
of					
2-hydroxy-2-	0.2	6.5	6.4	66.7	1.0
sulfinato-	0.4	6.5	6.5	67.2	1.5
acetic acid	0.6	6.5	6.6	67.6	1.9
corresponding	0.8	6.5	6.6	68.0	2.3
to Example 3	1.0	6.5	6.7	68.1	2.4

¹⁾ Compared with the untreated groundwood

Example 13

5 Deinked pulp bleaching

Conditions for the deinked pulp bleaching:

Stock consistency: 7.4%

Bleaching temperature: 75°C

10 Bleach addition: 0.2/0.4/0.6/0.8/1.0% of bleach,
absolutely dry

Bleaching time: 60 minutes

15 For the bleaching, 70 g of deinked pulp were in each
case weighed into polyethylene bags. To add the bleach,
aqueous solutions were prepared (1 ml of these
solutions comprised 0.2% of each bleach absolutely
dry). After the bleach solution had been pipetted in,
the bags were immediately tied up, and the contents
were thoroughly mixed by kneading the closed bags. The
20 bleaching temperature was regulated using a thermostat

(water bath).

After the required bleaching time, the pulp slurry was transferred to measuring flasks and the pH after
5 bleaching was measured. The volume was then made up to 300 ml with tap water and the mixture was homogenized by stirring the pulp slurry. The sheets were formed using a customary suction sheet former using the entire pulp slurry. The resulting sheets were vacuum-dried in
10 the sheet former for 15 minutes.

The whiteness R457 of all of the sheets formed was determined using a whiteness measuring device (Elrepho 2000 from Datacolor). The results are summarized in
15 Table 5.

Table 5

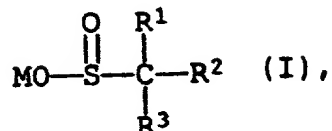
Bleach	Amount of bleach [% absolute ly dry]	Initial pH	Final pH	Whiteness	Whiteness increase ¹⁾
	0.0	7.2	7.2	64.5	-
Sodium	0.2	7.2	7.2	65.9	1.4
formalde-	0.4	7.2	7.3	66.3	1.8
hyde	0.6	7.2	7.3	66.9	2.4
sulfoxylate	0.8	7.2	7.3	66.9	2.4
	1.0	7.2	7.4	67.0	2.5
Disodium salt	0.0	7.2	7.2	64.5	-
of					
2-hydroxy-2-	0.2	7.2	7.4	64.9	0.4
sulfinato-	0.4	7.2	7.4	66.0	1.5
acetic acid	0.6	7.2	7.4	66.2	1.7
corresponding	0.8	7.2	7.5	66.5	2.0
to Example 3	1.0	7.2	7.5	66.3	1.8

¹⁾ Compared with the untreated deinked pulp

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We claim:

1. A sulfinic acid compound of the formula (I)



5 where

M is a hydrogen atom, an ammonium ion, a monovalent metal ion or an equivalent of a divalent metal ion of the groups Ia, IIa, IIb, IVa or VIIb of the Periodic Table of the Elements;

R¹ is OH or NR⁴R⁵, where R⁴ and R⁵ independently of one another are H or C₁-C₆-alkyl;

R² is H or an alkyl, alkenyl, cycloalkyl or aryl group, it being possible for these groups to have 1, 2 or 3 substituents which are chosen independently of one another from C₁-C₆-alkyl, OH, O-C₁-C₆-alkyl, halogen and CF₃; and

R³ is COOM, SO₃M, COR⁴, CONR⁴R⁵ or COOR⁴, where M, R⁴ and R⁵ are as defined above, or, if R² is aryl, which may be unsubstituted or substituted as defined above, is also H,

and the salt thereof.

- 25 2. A sulfinic acid compound as claimed in claim 1 of the formula (I),

where

M is an ammonium or alkali metal ion or an equivalent of an alkaline earth metal ion or zinc ion.

- 30 3. A sulfinic acid compound as claimed in claim 1 or 2 of the formula (I),

where

R¹ is OH or NH₂.

4. A sulfinic acid compound as claimed in claim 1 of
5 the formula (I),

where

R² is a hydrogen atom or an alkyl or aryl group
which may have one or two hydroxyl or alkoxy
substituents.

10

5. A sulfinic acid compound as claimed in claim 1 of
the formula (I),

where

- R³ is COOM or COOR⁴, where M and R⁴ are as defined
15 in claim 1.

6. A sulfinic acid compound as claimed in claim 1 of
the formula (I),

where

- M is an alkali metal ion or an equivalent of an
20 alkaline earth metal ion or zinc ion;

R¹ is OH or NH₂;

R² is H or alkyl; and

- R³ is COOM or COOR⁴, M being as defined above and
25 R⁴ being H or C₁-C₆-alkyl.

7. A sulfinic acid compound as claimed in claim 4 of
the formula (I),

where

- R² is aryl, which may have one or two hydroxyl
30 or alkoxy substituents; and

R³ is H.

8. A sulfinic acid compound as claimed in claim 7 of
35 the formula (I),

where

R^2 is hydroxyphenyl or C_1 - C_4 -alkoxyphenyl.

9. A sulfinic acid compound as claimed in claim 1 of the formula (I),

where

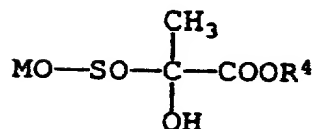
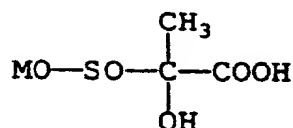
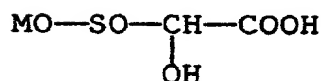
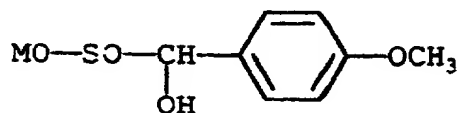
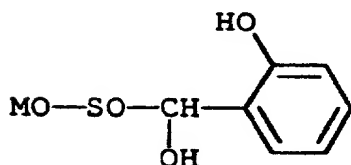
M is an alkali metal ion or an equivalent of an alkaline earth metal ion or zinc ion;

R^1 is OH or NH_2 ;

R^2 is hydroxyphenyl or C_1 - C_4 -alkoxyphenyl; and

R^3 is a hydrogen atom.

10. Compounds of the formulae (M = Na, K, Mg, Ca, Zn):



($R^4 = CH_3, C_2H_5$).

15

11. A mixture of a sulfinic acid compound as claimed in one of claims 1 to 10 with the sulfonic acid corresponding to the sulfinic acid compound or the salt thereof and with or without the corresponding sulfite.

20

12. A mixture as claimed in claim 11 having the following composition:

5	Compound of the formula (I)	20-99% by weight
	Sulfonic acid corresponding to	
	the compound of formula (I)	0-60% by weight
	M ₂ SO ₃	0-40% by weight

10 13. A mixture as claimed in claim 12 having the following composition:

	2-Hydroxyphenylhydroxymethylsulfinic	
	acid, sodium salt:	61-98% by weight
15	2-Hydroxyphenylhydroxymethylsulfonic	
	acid, sodium salt:	2-15% by weight
	Sodium sulfite:	0-37% by weight

20 14. A mixture as claimed in claim 12 having the following composition:

	4-Methoxyphenylhydroxymethylsulfinic	
	acid, sodium salt:	60-98% by weight
	4-Methoxyphenylhydroxymethylsulfonic	
25	acid, sodium salt:	2-15% by weight
	Sodium sulfite:	0-38% by weight

30 15. A mixture as claimed in claim 12 having the following composition:

	2-Hydroxy-2-sulfinatoacetic acid,	
	disodium salt:	40-73% by weight
	2-Hydroxy-2-sulfonatoacetic acid,	
	disodium salt:	2-7% by weight
35	Sodium sulfite	0-33% by weight

Water: 5-30% by weight

16. A mixture as claimed in claim 12 having the following composition:

5

2-Hydroxy-2-sulfinatoacetic acid,
zinc salt: 20-70% by weight

2-Hydroxy-2-sulfonatoacetic acid,
zinc salt: 5-60% by weight

10 water: 5-30% by weight

17. A mixture as claimed in claim 12 having the following composition:

15

2-Hydroxy-2-sulfinatopropionic acid,
disodium salt: 38-70% by weight

2-Hydroxy-2-sulfonatopropionic acid,
disodium salt: 5-30% by weight

Sodium sulfite: 0-33% by weight

20 Water: 5-30% by weight

18. A mixture as claimed in claim 12 having the following composition:

25

Ethyl 2-hydroxy-2-sulfinatopropionate,
sodium salt: 60-80% by weight

Ethyl 2-hydroxy-2-sulfonatopropionate,
sodium salt: 0-5% by weight

Sodium sulfite: 0-5% by weight

30 Water: 5-20% by weight.

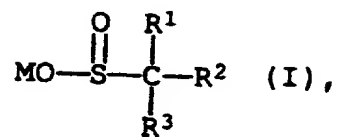
19. A composition comprising at least one sulfinic acid compound as claimed in one of claims 1-10 or at least one mixture as claimed in one of claims 11-18, together with customary additives and auxiliaries.

35

20. The use of the sulfinic acid compound as claimed in one of claims 1-10 as reducing agent.
- 5 21. The use as claimed in claim 20 as cocatalyst in emulsion polymerization or redox catalyst system in plastics production.
- 10 22. The use as claimed in claim 20 as reducing agent component for textile printing, in textile bleaching or vat dyeing or as reducing bleach for mineral refining or fiber finishing.

Abstract

The present invention relates to sulfinic acid compounds of the formula (I)



5

where the substituents are as defined in the description.

The novel sulfinic acid compounds can be used as
10 . reducing agents which do not eliminate formaldehyde.

DECLARATION AND POWER OF ATTORNEY FOR PATENT APPLICATION

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

SULFINIC ACID DERIVATIVES AND THEIR PREPARATION AND USE

the specification of which is attached hereto unless the following space is checked:

☒ was filed on _____ as United States Application Serial Number _____

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT international application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT international application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s):

	<u>Number</u>	<u>Country</u>	<u>Day/Month/Year Filed</u>
1.	197 43 759.1	Germany	02 October 1997
2.	PCT/EP98/04055	PCT	01 July 1998

I hereby claim the benefit under 35 U.S.C. § 119(e) of any United States provisional application(s) listed below:

	<u>Application Number</u>	<u>Filing Date</u>
1.		
2.		

I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT international application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT international application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 C.F.R. § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

	<u>Application Number</u>	<u>Filing Date</u>	<u>Status: patented, pending, abandoned</u>
1.			
2.			

I hereby appoint the following attorneys and agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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